Final Technical Report

STUDY OF AIR POLLUTANT DETECTORS

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PREFACE

The objective of this research program was the evaluation of mass spectrometry as a total air pollutant detector. The program was supported by the National Aeronautics and Space Administration, Ames Research Center, Moffet Field, California. Dr. Walter Starr was the technical monitor for NASA.

This report summarizes the work done during the duration of the program. The work was performed in the Physics Department at the University of Missouri - Kansas City. Mr. Paul Gutshall and Mr. Quinton Bowles served as principle investigators. They were assisted by Drs. Paul Bryant and Orville Weddle. Mr. Gil Radolovich, a graduate student, also contributed to the research efforts.

The University would like to express appreciation to NASA for support of this program.

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I. SUMMARY

The objective of the research efforts described in this report was to apply field ionization mass spectrometry to the detection of air pollutants. Since air samples are primarily composed of nitrogen, oxygen, carbon dioxide and water vapor, there was a need for a reduction of the level of these gases compared to the quantity of pollutants. The original approach proposed to accomplish this was to use a series of dimethyl silicone membranes to enrich the relative level of pollutants. Published permeation data, as well as previous studies indicated this approach was feasible. The use of field ionization mass spectrometry was desirable because of the simplified spectrum obtained as compared to the normal electron impact mass spectrum.

The membrane enricher was designed and evaluated during the program. Repeated attempts to obtain the desired enrichment using the membrane enricher were unsuccessful. Although enrichment of pollutants did occur, the level was not sufficient to allow detection of trace contaminants in the environment. We were able, using the membrane enricher to detect sulfur dioxide in a mixture of 10 ppm of SO_2 in air. A study of a three stage membrane enricher was undertaken to determine the enrichment per membrane. It was found that the enrichment occuring across the first membrane agreed with the value obtained from the manufacturer. Our measured value for sulfur dioxide was 35 compared to 25 as reported by General

Electric. However, the enrichment occuring across the second stage was considerably below those observed at the first stage. This data is summarized in Table II.

After an evaluation of the dimethyl silicone rubber membrane showed this approach was not feasible, a second enrichment process was evaluated. This method used an open pore polyethylene foam as a selective adsorber. The foam works on the principle that different materials have different adsorption energies on similar materials. Previous studies on foam adsorbers have shown that the heavier molecules, such as the hydrocarbons can be removed from the air by adsorption. Although we were not able to do extensive study of the foam adsorber system, the results that were obtained were encouraging. Air samples were collected by passing ambient air through the foam adsorber. Analysis of the adsorbed material on the foam indicates the presence of several contaminants, which can be correlated to products of internal combustion gasoline engines. This data is summarized in Section IVB.

Field ionization mass spectrometry, as an analytical tool for air pollution detection was also evaluated during the research program. A commercial mass spectrometer (Varian Mat SM1-B) was used to analyze the samples. Because of the complex spectrum one obtains when electron impact ionization is used, a field ionization source was chosen as a method of producing ions. The resulting mass spectrum consists of primarily molecular ion peaks with a minimum of fragment peaks. However, the use of field ionization

results in a loss of sensitivity. For the spectrometry used in our laboratory, the reduction in sensitivity is approximately 100 when going from electron impact to field ionization. The problem of sensitivity was overcome by using standard ion counting techniques.

In summary we feel that the membrane enricher system is not a suitable method of removing air pollutants from atmospheric air. Although the enrichment obtained with the membranes can be enhanced by adjusting parameters such as pressure, temperature and geometry, we feel the final result will still be undesirable. On the other hand, the foam adsorber-field ion mass spectrometer approach does show promise as a useable system for air pollution detection. It is the feeling of the investigators that further development of this system can lead to a total air pollution detection system.

II. INTRODUCTION

The objective of the research program under NASA Contract
NAS2-7078 was to apply field ionization mass spectrometry to the
detection of air pollutants. The Physics Department, University
of Missouri-Kansas City has been conducting research in the area
of trace gas analysis for several years. These research efforts
led to the research reported herein.

The identification of many materials which are harmful to man
and his environment have been made during the past decade. The
maximum allowable concentrations of these materials in the atmos-
phere have also been established by various governmental agencies.[1]
The contaminants of most concern can be listed in one of the follow-
ing classes: fixed gases; sulfur compounds; nitrogen oxides;
hydrocarbons; and particulates (aerosols).[2] A review of the
current methods of measuring the above contaminants is presented
below.

1. Fixed gases - nitrogen, oxygen, carbon dioxide and carbon
   monoxide are included in the fixed gases. Orsat analysis
   is a common method of detecting the fixed gases. In this
   process the gas sample is passed through selective absorbers
   and the decrease in gas volume (at constant pressure and
   temperature) is measured. The decrease in volume of the
   gas can then be related to a specific material. Gas

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chromatography and infrared spectrometry are also standard
methods of analysis for the fixed gases.

2. Sulfur compounds - SO_2, SO_3, H_2S and the mercaptans are the
    major sulfur compounds contributing to the contamination of
    the environment. SO_2 was one of the earliest recognized
    pollutants in the atmosphere. Furthermore, the large amounts
    of SO_2 admitted into the atmosphere by industrial processes
    have made SO_2 detection a critical need. A large number of
    SO_2 detectors are available[3/] and the techniques they employ
    generally fall in one of the following types: UV absorp-
    tion; correlation spectrometry; conductometric analysis;
    electrochemical analysis; and flame photometric analysis.
    Wet chemical analysis is used to detect many of the sulfur
    bearing compounds in the atmosphere. However most of the
    wet chemical systems are total-sulfur analyzers, thus
    making it difficult to determine which particular compound
    is the pollutant.

3. Nitrogen oxides - nitric oxide (NO) and nitrogen dioxide (NO_2)
    are the main pollutants in this group. The method most
    commonly used to detect NO and NO_2 is the phenoldisulfonic
    acid analysis. The gas sample is mixed with a dilute solu-
    tion of a sulfuric acid-hydrogen peroxide mixture. The NO
    and NO_2 are reduced to nitric acid by reaction with the
    hydrogen peroxide, and nitric acid is then measured by
    colorimetric analysis. Although other methods are used

the phenoldisulfonic acid analysis is generally considered
the more accurate and reliable.

4. <u>Hydrocarbons</u> - Detection methods employed for monitoring
hydrocarbon levels are divided into two types according to
their objectives: total hydrocarbon content assessment;
and, individual chemical species measurements. The flame
ionization detector is used to measure the total hydro-
carbon content of a gas sample. Gas is ionized in a hydrogen-
air flame and the ion intensity is measured using an electro-
meter or electron multiplier system. The number of ions
generated is proportional to the total hydrocarbon content
of the gas. Individual hydrocarbon species are normally
measured by means of standard gas chromatographic techniques.
Either mass spectrometry or flame ionization methods may
be employed as detectors for the GC column.

5. <u>Particulates</u> - Solid particles as well as liquid aerosols
are the pollutants in this class. There are two general
methods of measuring particulate matter in the atmosphere:
optical transmission measurements; and, mass determination.
The optical transmission measurements (opacity) correlate
the amount of light passing through the gas species to the
particulate matter contained in the specimen. Particulate
content is related to light transmittance of the gas by an
arbitrary scale, called Ringelmann numbers. The Ringelmann
numbers start at zero, indicating 100 percent transmittance

of the incident light, 1 indicating 80 percent transmittance
of the incident light, etc. Mass determination methods of
detecting particulates are normally used for large emission
values, such as those from smoke stacks. This method requires
that a known volume of gas be drawn through a filter at a
constant velocity. The filter is then weighted and the par-
ticulate content of the gas is calculated. Other methods
include the use of piezoelectric crystals. The resonance
frequency of the crystal changes as weight is added to the
crystal. Therefore particulate matter deposited on the
crystaline surface can be correlated to the shift in the
resonance frequency.

The above discussion is a brief review of the techniques and
methods for the detection of air pollutants. In some cases, there
are disagreements among authorities as to the most desirable method
for detection of a particular pollutant. A detection method which
could be applied to several, if not all, pollutants would be de-
sirable.

Mass spectrometry not only possesses the require sensitivity
for trace gas analysis, but also can be applied to all gaseous
pollutants found in the air. However, several basic problems pre-
vent direct application of mass spectrometry to the analysis of
complex air mixtures at full atmospheric pressures. Analysis of
an air sample at atmospheric pressure requires reducing the sample
pressure to the operating level of the mass spectrometer (approxi-

mately 10^{-5} Torr). Thus an air pollutant existing at a level of 1 ppm in air would be reduced to 10^{-11} Torr in the mass spectrometer. A method of separating the pollutants from the major air gases (nitrogen, oxygen, etc.) before the sample was analyzed would overcome the above problem.

Two such enriching devices were investigated during this program. The first method studied was the dimethyl silicone rubber membrane separator. Although the silicone membrane separator has some limited applications to trace gas analysis, in the authors opinion, it is not desirable as a general mass spectrometry enriching system. The second method investigated was the use of a selective adsorber made from polyethylene foam. From our experience the foam absorber has the necessary properties to serve as an enriching device for atmospheric air pollution studies.

Two methods of ionization were used in our air pollution studies by mass spectrometry. Electron impact ionization, as commonly used in most mass spectrometers, renders relatively high sensitivity values. However, the molecular ion is fragmented into several ions of smaller mass making the interpretation of the mass spectrum difficult. Field ionization eliminates nearly all of the fragmentation in the spectrum, thus simplifying the interpretation of the data. Both types of ionization were used during this research program.

III. EXPERIMENTAL PROCEDURES

Three areas of technology are described in this section. Each is sufficiently unique to warrant a review of the developments and the contributions made during this research program.

The application of field ionization mass spectrometry to air pollution analysis is described first. The advantages and disadvantages of that technology have been determined. The calibration data for a number of pure gases has been recorded along with the specificity which can be realized with the field ion mass spectrometer technique.

The application of membrane separation to air pollution studies is described second. The dimethyl silicone membranes exhibit various permeability rates for different gases. Thus the action of the separator may be described as a relative enrichment process. The design and operation of the membrane separators to achieve the necessary enrichment for trace gas analysis from air samples has been thoroughly investigated. A review of the applications and the sensitivities obtained with the membrane separators is given.

A. Field Ionization Mass Spectrometry (FIMS)

The application of FIMS technology to the analysis of air pollutants has shown some advantages and some disadvantages. The technology has proven advantageous for the overall analysis of a complex gas mixture such as air since a much simpler and unambi-

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guous pattern is produced. It has also been noted, however, that the sensitivity of the field ionization process is lower than for the electron impact technique which is a disadvantage for trace analysis applications.

The application of FIMS to air pollution has been developed and improved in several areas. The ionizer itself is unique[4/] in that the ionizer element consists of graphite which is inert to chemical reactions with the materials being analyzed. Since the field ion source operates without heating at ambient temperatures the graphite is even inert to pure oxygen. In addition to the lack of thermal or catalytic cracking, which a hot filament produces, this special field ionizer design also avoids the cracking normally produced by other field ionizer designs. Even though the other designs have shown a marked improvement over the electron impact process in regard to the production of cracking patterns they still generate considerable ambiguity when applied to the very complex mixture of polluted air. In particular, the presence of large hydrocarbon molecules in air provides the source for many fragment peaks.

Other field ionizer designs require an activation coating process to bring their ion yield values up to useable levels. However, the special graphite filament system does not require activation to produce even higher (by a factor of two or more) ion yields for the same gases and conditions as the activated ionizers. The activation

of the other sources does cause a large spread in the operating elec-
tric field strength values from below threshold level for ionization
(approximately 10^8 V/$\overset{o}{A}$) up to the critical value of about 4.5×10^8 V/$\overset{o}{A}$.
Thus, ions may be fragmented by the high-to-critical field strength
values. That is, an ion is polarized in the field and stretched
to the breaking point by a value above the moderate range. The
special graphite ionizer design avoids this mode of ion fragmenta-
tion by avoiding the sharp overgrowth deposits which constitute the
activation layer. Since the graphite need not be activated with
dendrites grown from the decomposition of organic vapors it does
not suffer from the consequences of a large range of field strength
values. The surface of the graphite filament has small steps due
to the lamellar graphite structure. Since the layer planes are
rolled into a scroll-like filament rather than being flat as in a
normal graphite crystal the layer steps are distributed over the
entire surface area of the cylindrical filament. Pertibations of
the electric field caused by the layer steps are not nearly as great
as those caused by the large activation overgrowth which are necessary
for other field ionizer designs. The narrow spread in the electric
field strength values generated by the smoother graphite ionizer
allows this design to be operated in the moderate field strength
range, above threshold for ionization, but with no part at the
critical value which would cause fragmentation.

The above theory of field ionizer operation had been tested
and verified previously with many pure gases. The spectra obtained

did not show cracking due to the ionization process for any of the compounds tested. A few large non-volatile materials suffered thermal cracking from the process of evaporating them from a liquid or solid phase into the mass spectrometer as a gas.

The avoidance of cracking by the ionization process or by a hot filament is necessary if a mass spectrometer is to be applied directly to air pollution analyses. Detectable quantities of compounds exist at every atomic mass number across the range of volatile compounds so that ambiguity is produced if the original compound forms are broken into multiple fragments. The FIMS technology applied here has shown the ability to analyze a gaseous mixture without producing abiguous results.

B. The Membrane Separator

The membrane separator which was initially employed is shown in Figure 1 and is based on a design obtained from Dr. John Hobbs of the Department of Transportation. The sample connected at the inlet flange is drawn across the first membrane by a differential pressure created by a 0.5 cfm mechanical vacuum pump connected at (A). A pressure of 200 Torr was maintained at the front face of the first membrane. The pressure between the first and second membrane is maintained at approximately 90 Torr and the pressure between the second and the third membranes is maintained at approximately 2×10^{-3} Torr. This is accomplished by a second 0.5 cfm mechanical vacuum pump attached at point B. The variable conductance valves indicated at 3 and 4 were adjusted to maintain these pressure differentials. Pressure is monitored by three thermocouple vacuum
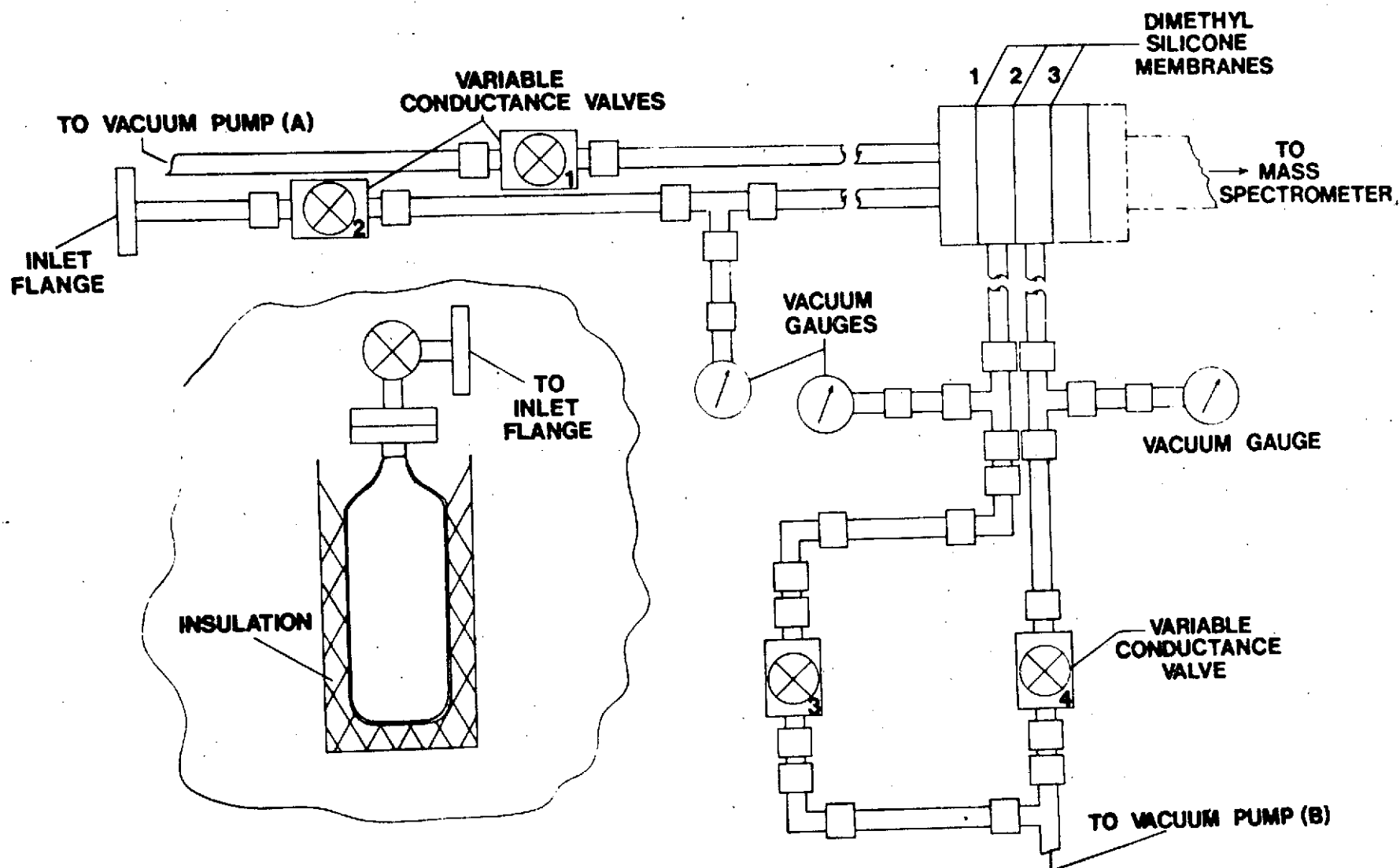
Figure 1 - Schematic diagram of the dimethyl silicone membrane separator.
The three stages allow the gas pressure to be reduced from
one atmosphere to 10^{-5} torr.

gauges at the point shown. The entire assembly is connected to the mass spectrometer through a final vacuum flange and a line of sight insertion probe. Some of the preliminary data obtained with the membrane separator will be discussed in Section III.

Calculations using permeability factors published by [*]General Electric indicated enrichment factors much greater than we were able to measure. Therefore a more fundamental investigation of the permeability through the membranes was undertaken during the fourth quarter.

Figure 2 is a schematic diagram showing the membrane enricher and its attachment to a quadrupole mass spectrometer. The operation of the system is explained by assuming that the entire apparatus is under vacuum pressure up to valve number 1 on the sample tank. To date we have been able to reach a vacuum of 10^{-7} torr in the entire system. If we now wish to make a spectrum of the sample tank directly then we must open valve 1, valve 4, and valve 5. Then by opening valve number 6 which is a high sensitivity variable leak valve we are able to raise the pressure in the quadrupole to 6×10^{-6} torr. Next by closing valve 5 and valve 4 and opening valve 2 it is possible to flow the sample by the face of the first membrane as shown. Note that we have inserted a splitter which forces the sample to pass entirely in front of the membrane through

[*]Dimethyl silicone rubber membranes were obtained from the Medical Development Operation - Chemical and Medical Division - General Electric Corporation.
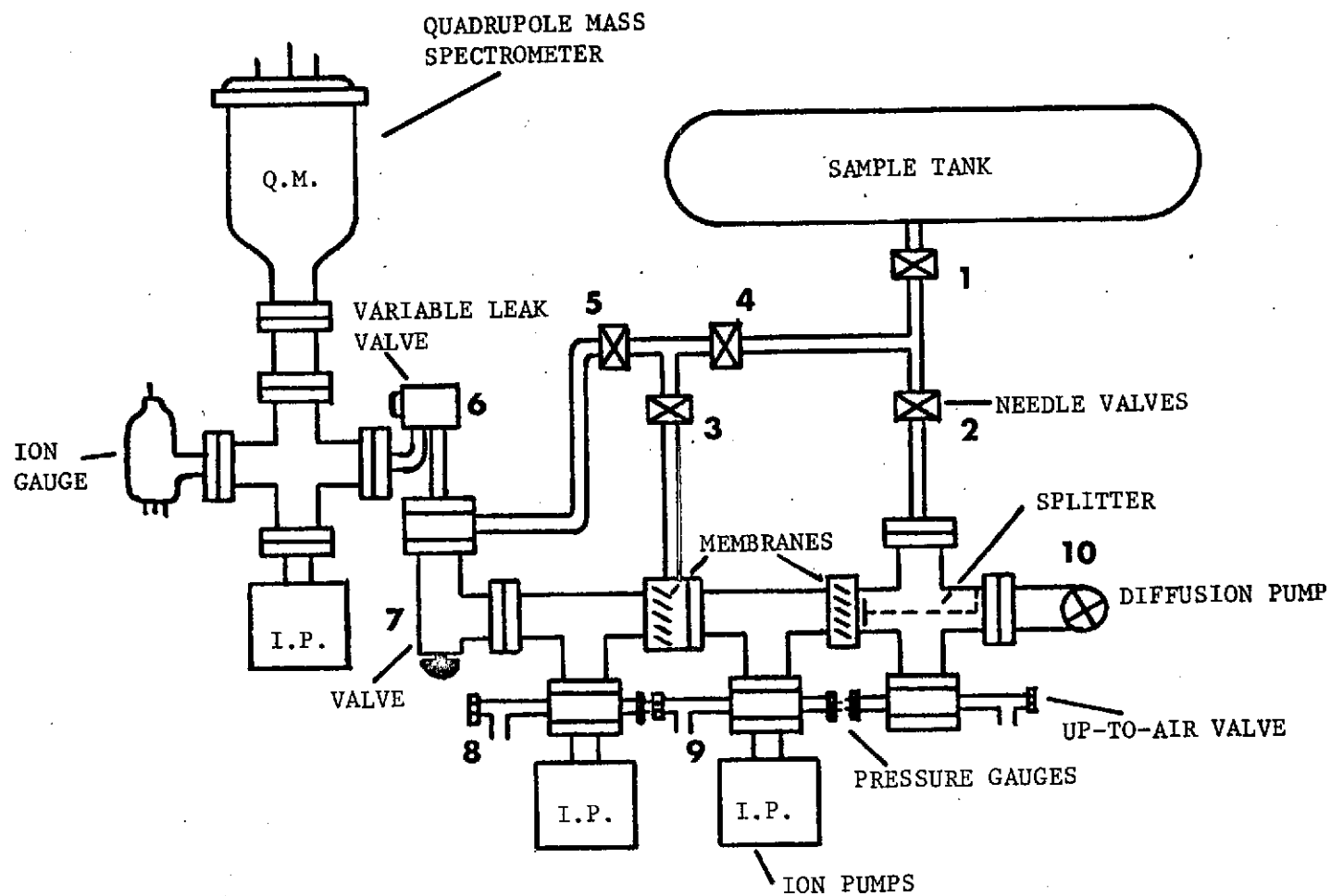
Figure 2. Experimental equipment showing quadrupole mass spectrometer with two stage membrane separator.

the slight constriction shown. After evacuating the small portion

of line between valve 6 and valve 7 we can now evaluate the enrich-

ment across the first membrane by opening valve 3 and valve 5 which

will allow first stage enrichment gas to flow into the small re-

servoir between valve 6 and 7. Again by evacuating the small re-

servoir, closing valve 3 and 5 and then opening valve 7, we are

able to sample the gas mixture after two stages of enrichment. In

this manner we monitor, at any point in time, the degree of enrich-

ment which has occurred through the rubber membranes. It will be

noticed that only two stages of the separator are shown, however

it was felt that a third stage could be added any time that satis-

factory results were obtained across two membranes. In the arrange-

ment shown we are using ion pumps rather than diffusion pumps to

provide the necessary vacuum integrity.

C. Polyethylene Foam Adsorber System

    1. Foam Absorber

The adsorber consists of an open pore polyethylene foam with

an average pore size of 100 microns. The wall thickness is about

5 microns. The open porosity allows air to be drawn through the

foam with maximum interaction of the gas with the walls. The

principle by which the foam works is simply one of allowing those

gaseous constituents with high absorption energies, such as oxygen

and nitrogen, to pass through the foam largely undisturbed. How-

ever, those contaminating constituents such as hydrocarbons are

absorbed on the walls and within the pores of the foam.

The foam was manufactured in a disk, 15 cm in diameter and 2 cm thick. Small disks, 2.5 cm diameter and 1 cm thick to be used for collecting samples, were cut from the larger disks. After reducing the foam to the approriate size, it was placed in an ultra high vacuum system and degassed at elevated temperatures (100° C). The 24 hours degassing procedure removed any absorbed material which may have been present in the foam either from the manufacturing process or from previous experiments if the foam disk was being recycled. The vapor pressure of the foam after the vacuum processing was 10^{-7} Torr or lower.

2. Sample Collection System

The sample collection system, utilizing the foam adsorber, is shown schematically in Figure 3. The overall dimensions of the collecting system are 12 cm by 10 cm. A rubber gasket is used to seal the edge of the foam, thus insuring that the gas flow is through the foam rather than around it. A small fan (115 cfm) was used to force air through the adsorber. The collection system is small and portable, requiring only access to a 110 volt source from which to power the fan.

The collection system was initially cleaned by out gassing the system (excluding fan) in a vacuum chamber. To reduce any contamination that might originate from the fan motor, the air flow direction was from the foam to the fan.
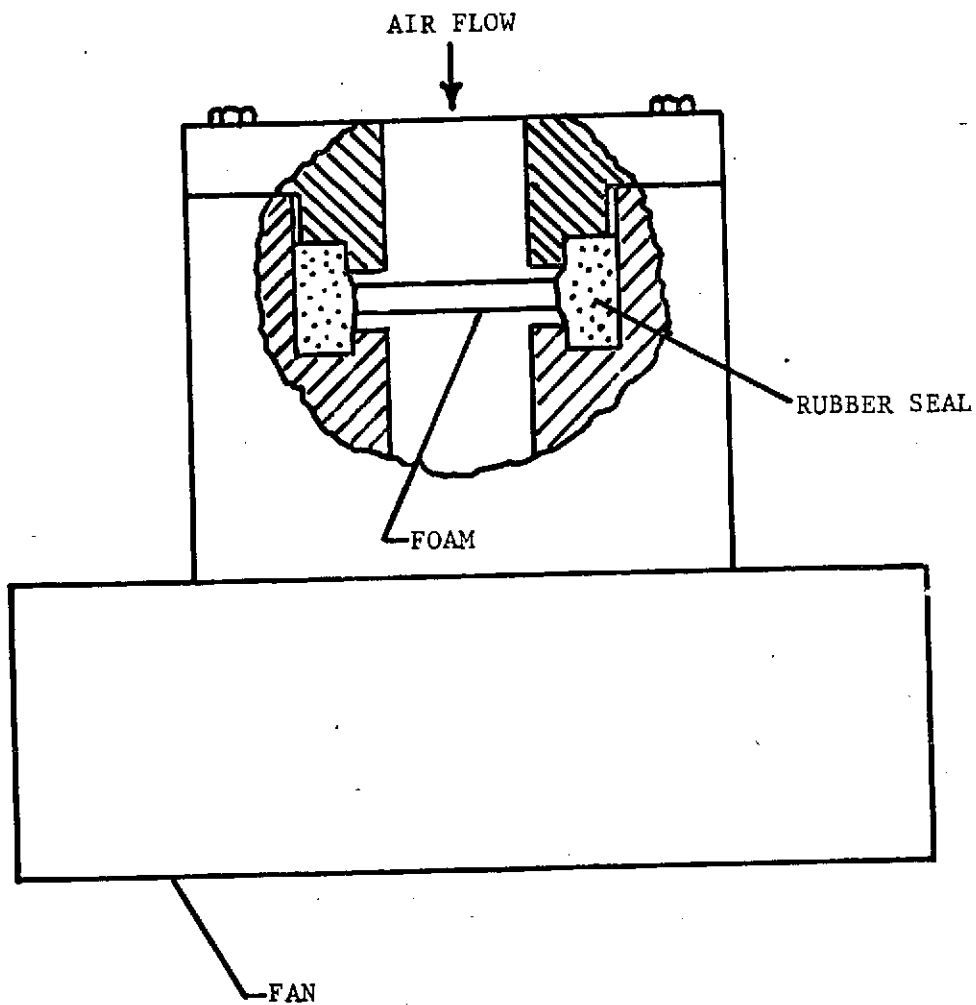
AIR FLOW

RUBBER SEAL

FOAM

FAN

Figure 3. Air sample collection system using a foam adsorber.
Air is moved through the foam by a fan.

3. Sample Processing

After the foam absorber had been exposed to the gas sample, the foam disk was removed from the collection system. The foam was then placed in a vacuum system to be processed prior to analysis (Fig. 4). The processing consisted of pumping on the foam to remove the nitrogen, oxygen, etc., from the foam pores. This initial evacuation required from 5 to 15 minutes and the final pressure was less than 10^{-6} Torr. At this point, the foam was isolated from the processing vacuum system.

The foam was allowed to remain in the closed chamber for 15 minutes. The foam was then exposed to the mass spectrometer by opening a valve between the foam chamber and the mass spectrometer. A line of sight probe was used to connect the foam chamber to the mass spectrometer. The SM1-B mass spectrometer with the foam processing system in position is shown in Figure 5. A mass spectrum was taken immediately following exposure of the foam to the mass spectrometer. Experience has shown that repeated spectra can be obtained on a single foam by simply allowing the foam to set isolated for 15 minutes between mass spectrometry scans.
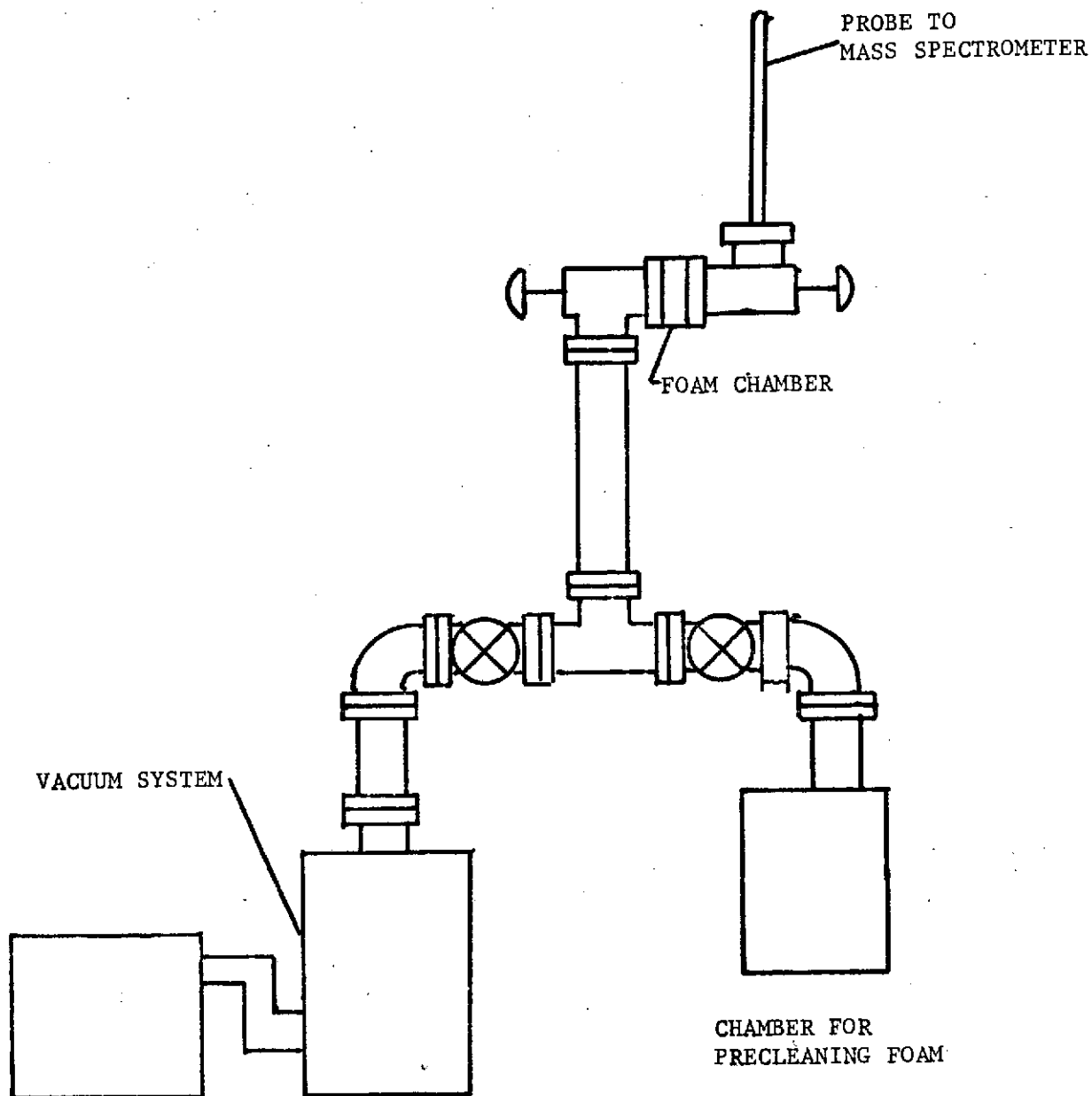
Figure 4.   Foam chamber and processing system for analysis of adsorbed gases. Valves on either side of foam chamber allow isolation of foam prior to exposing foam to mass spectrometer.
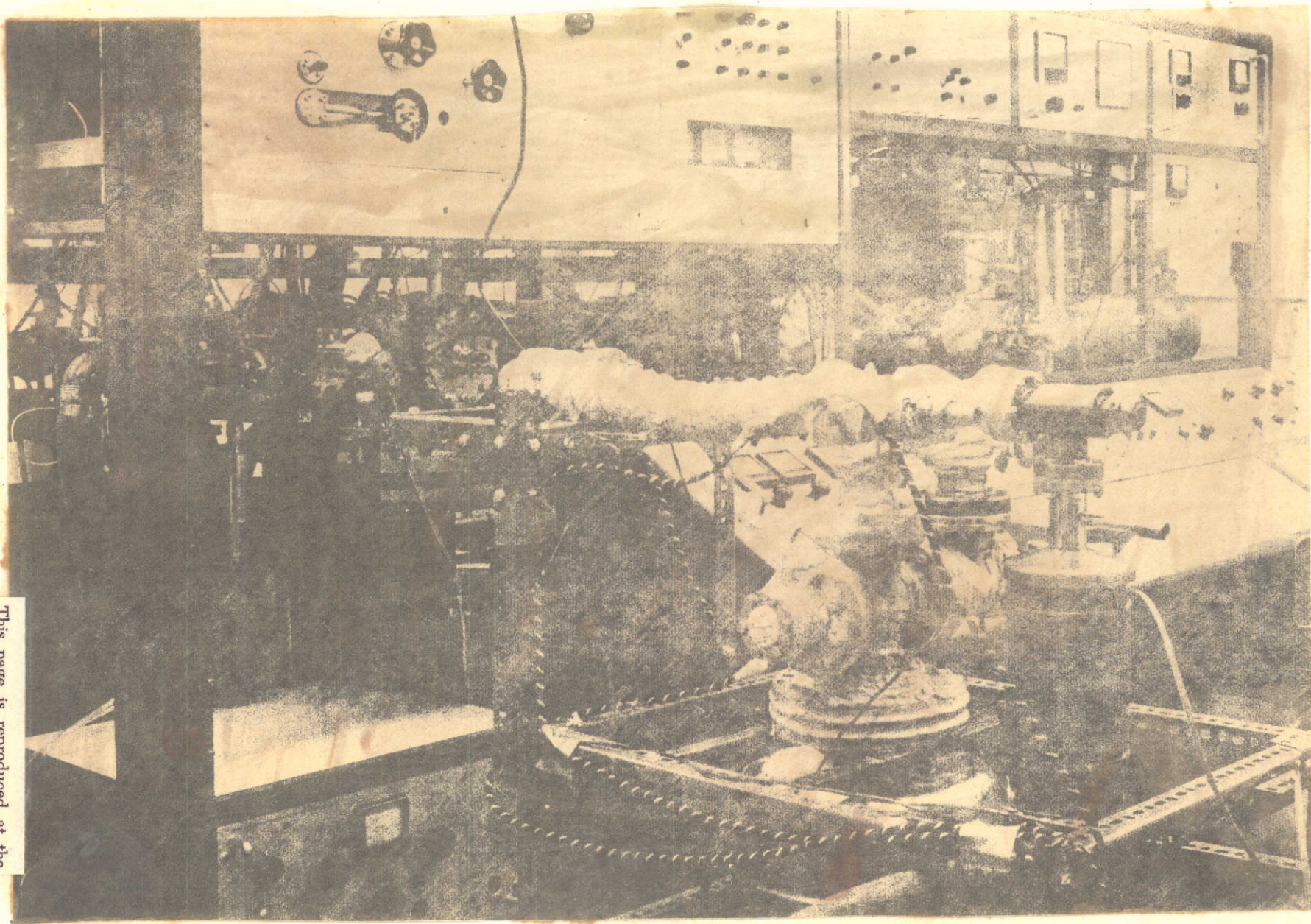
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Figure 5. Foam adsorber processing system attached to the mass spectrometer. Prepumping on the loaded foam removes nitrogen, oxygen and water vapor from the adsorber.

IV. EXPERIMENTAL RESULTS

A. Dimethyl Silicone Rubber Membranes

One of the difficulties encountered throughout the contract period was in obtaining membrane enrichment factors which were expected from the permeation rates published by the manufacturer for the dimethyl silicone rubber membranes. In addition the enrichment factors which we did obtain were not always repeatable from one day to the next.

Consequently, during the latter part of the contract period we decided to begin a rather basic study of the permeation characteristics of the membranes in addition to the main effort on the foam system.

The membrane system was assembled as shown in Figure 2 and attached to a Finnegan Instruments quadrupole mass spectrometer. The purpose of this change was to provide more detector sensitivity and shorter shut down – start up time if changes needed to be changed.

The first experiments conducted consisted of measuring the actual permeativity constants for several gases as shown in Table I. The measurements were made by the time lag method[5,6/]. This process requires that the low pressure sample volume is known rather accurately. Then the rise in pressure on the down stream side of the membrane is plotted as a function of time. When a

Table I.   Measured Permeability Constants P_r For Several Gases

Gas	Measured P_r (*)	Published P_r (**)
He	9.68	30
CO	10.19	30
C_2H_4	18.83	115
CO_2	34.0	270
O_2	188	50
SO_2	9463	1250
N_2	116	28

(*) $P_r = \dfrac{cc(R.T.P.) - cm}{cm^2 - sec - cmHg(\Delta P)} \; X \; 10^{-9}$

(**) Values published by General Electric Company for Dimethyl Silicone Rubber.

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steady state portion of the curve is reached, one can then take the average of two pressure readings from the linear portion of the curve, the known volume and the time and determine the actual flow in cc's of gas across the membrane. The actual permeativity constants were somewhat lower than those published by other workers, furthermore the ratio of permeativity constants which is a measure of enrichment for any combination of gases was not as great as that suggested by the General Electric data sheet.

Our first efforts at measuring enrichment were conducted on a pure mixture of oxygen and SO_2 with the fraction of SO_2 being about 15 percent. In this case we were able to demonstrate an enrichment factor of approximately 35 for SO_2/O_2. A range of enrichment factors for both stages 1 and 2 are shown in Table II. This data demonstrates the variations in enrichment obtained as a function of system pressure. Although this data is inconclusive the authors feel that it demonstrates the presence of an unknown factor involving the pressure and rate of supply of sample to the face of the membrane.

The presence of the large mass 28 peak which dominates the entire spectrum even in the absence of any supply of nitrogen (mass 28) proved to be quite disturbing. However, we now conclude that it originates as evolved gases from the ion pumps which are being used. This fact was determined by monitoring the entire spectrum on an oscilloscope during introduction of a sample to the quadrupole. Initially one could observe a rapid rise in the

Table II. Enrichment Factors For O_2-SO_2 Mixtures

Sample Number	Direct Sample (Inlet)		Stage 1 Enrichment		Stage 2 Enrichment		Total Enrichment	Pressures Used (X 10^{-3} Torr)		
	O_2	SO_2	O_2	SO_2	O_2	SO_2	SO_2	Inlet	Stage 1	Stage 2
1	90%	10%	21%	79%	—	—	34 times	2,000	250	—
2	80%	20%	19%	81%	8%	92%	45 times	1,500	350	180
3	85%	15%	51%	49%	24%	76%	17.9 times	100,000	550	200

major spectrum peaks (32, 48 and 64) corresponding to oxygen, and

SO_2 and then some seconds later one would observe a rise in mass 28

peak which would eventually increase beyond the height of the

mass 32 peak. A second test was conducted whereby the temperature

of the ion pump was raised by a heater and again the spectrum in-

dicated a gradual rise in the height in the mass 28 peak.

Table III represents the data obtained during the efforts to

show enrichment of atmospheric air constituents. We have shown only

the values of mass 18, 28, 32 corresponding to H_2O, N_2 and O_2.

Here again we observe the great discrepancy in the ratio of the

mass peaks corresponding to N_2 and O_2 and again we conclude that

problem originates with the evaluation from the ion pump used

to evacuate the mass spectrometer chamber. It is clear that enrich-

ment of the H_2O level has occurred but again the ratios are not as

great as predicted.

B. Selective Foam Absorber Data

Results obtained by applying the special polyethylene absorber

to the collection and processing of air pollution samples are re-

ported below. The results confirmed the ability of the foam to act

as an enricher for organic molecules and other large molecules in

relation to the main air constituents N_2, O_2, and CO_2. The ability

to collect a significant amount of sample from all various molecules

across the mass range of interest was also confirmed. The ability

to collect remotely, to transport, and to store samples for an

indefinitely long time was observed. Rapid processing of samples

Table III.   Relative Peak Heights of Four Atmospheric Components Thru
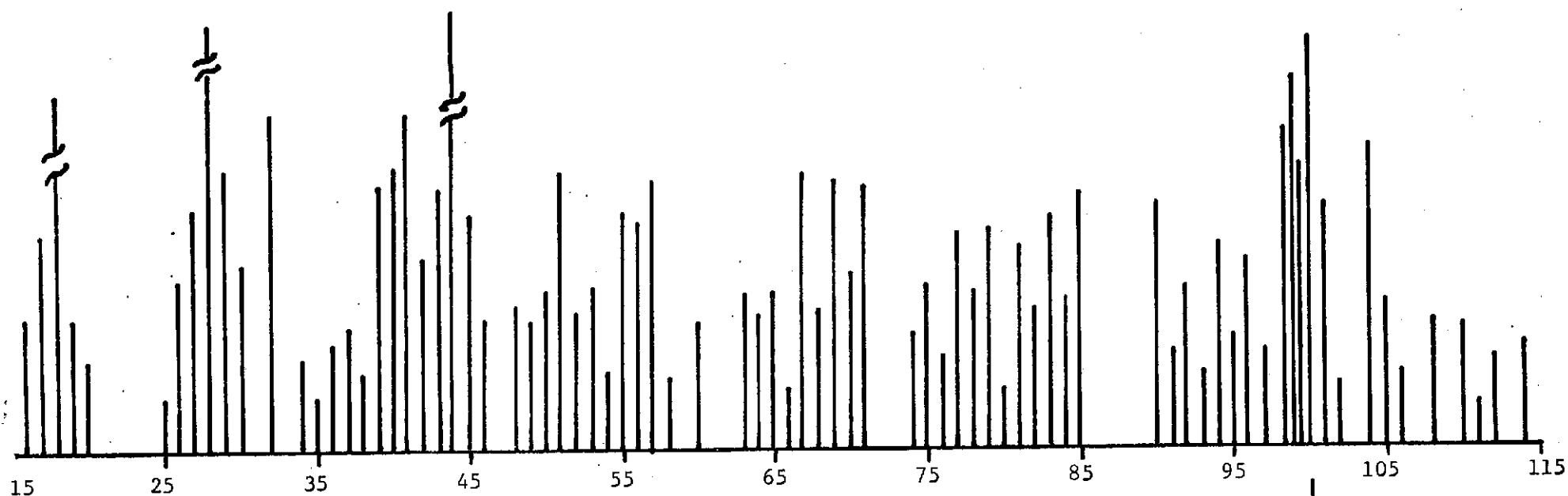One Membrane. (Based on a.m.u. 28 = 100%)

Atmosphere Sample Number	Direct a.m.u.				Thru One Membrane a.m.u.				Pressures Used $(X\ 10^{-3}$ Torr) Inlet	Stage One
	18	28	32	44	18	28	32	44		
1	3.93	100	3.37	—	36.8	100	2.4	0.6	1,000	2
2	0.7	100	2.45	—	3.4	100	4.4	0.24	760,000	1,200

was accomplished within five minutes. The water vapor level and the quantities of N_2, O_2 and CO_2 were reduced so that the mass spectrometer analysis could begin within five minutes from the introduction of a new sample to the analyzer system.

The application of the polyethylene foam to air pollution analysis was checked with both electron impact and field ion mass spectrometry. Background spectra were also recorded to determine the contribution to the final air pollution spectra from the polyethylene foam and the system itself. Since a significant contribution to the roadside air pollution sample came from automobile exhaust, a control spectrum for gasoline and its components also was recorded. These relevant background and control spectra are shown along with an air spectrum from an auto repair garage (see Fig. 6, 7, and 8).

The background spectrum, Fig. 6, was obtained with the use of the standard electron impact source which produces a somewhat higher sensitivity and a greater number of peaks due to the cracking process. Thus the spectrum shows a group of peaks from the m/e value of 98 to 102. This group of peaks arises from the presence of a low partial pressure of mercury in the mass spectrometer. The origin of this mercury background is obviously due to the use of mercury as the working fluid in the three diffusion pumps employed on the source, analyzer, and detector stages of this high resolution spectrometer. Even though liquid nitrogen traps are maintained above each pump there is still a detectable
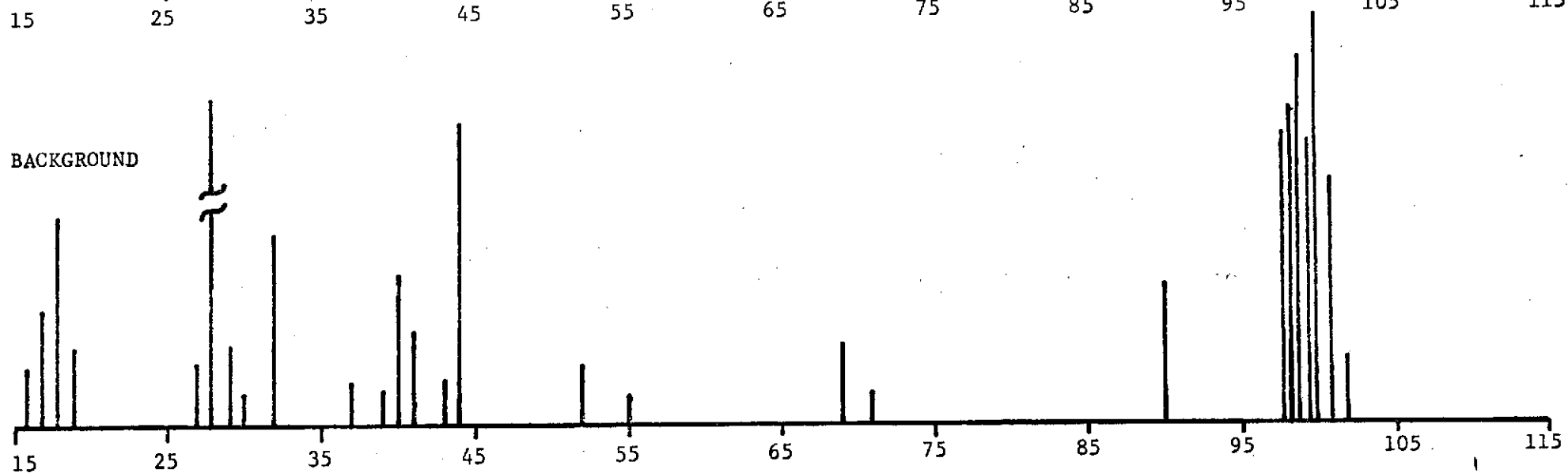
Figure 6.   Electron impact mass spectrum of air sample (top) and foam background (bottom).
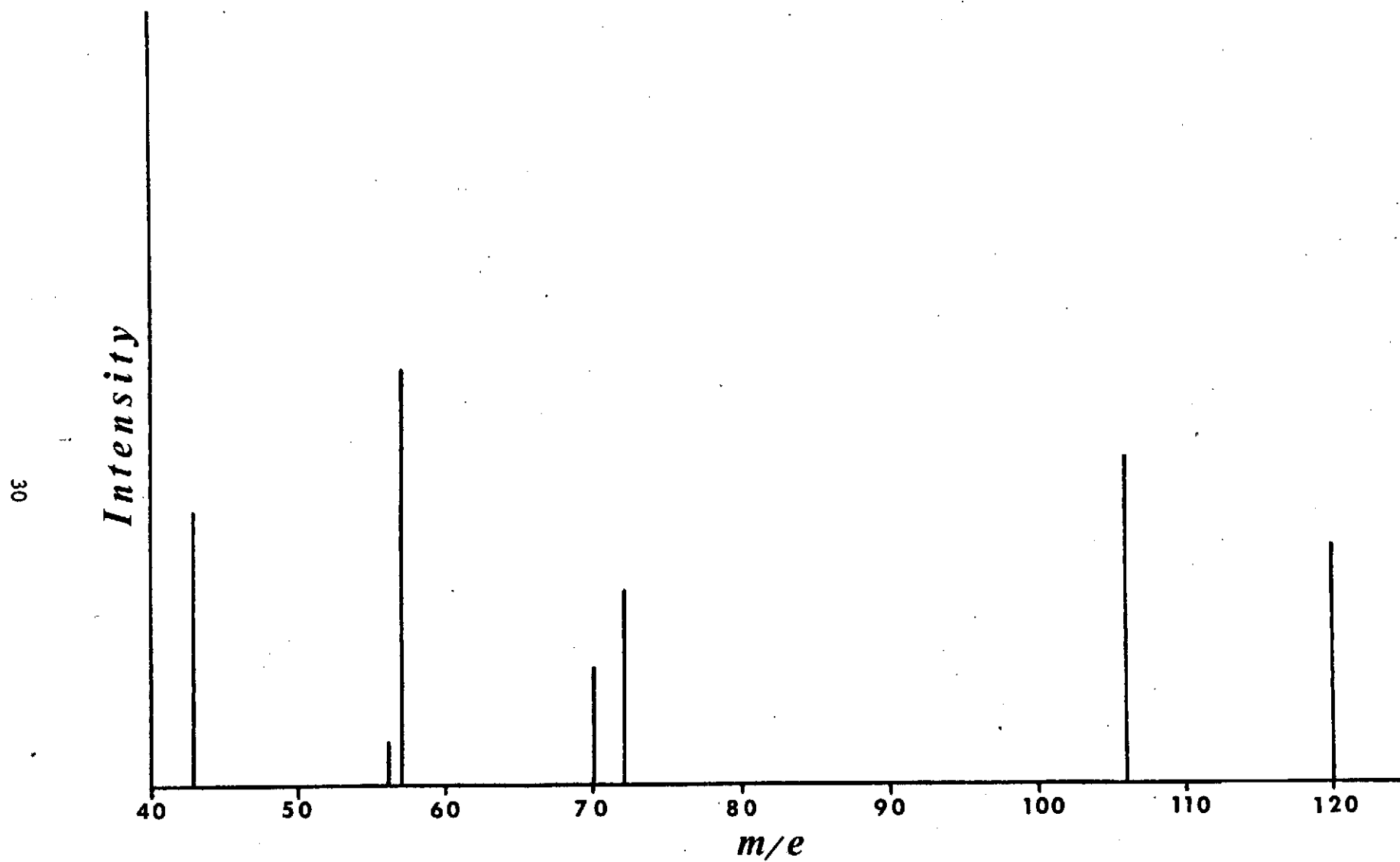
Figure 7. Field ion mass spectrum of gasoline admitted into the mass spectrometer through the liquid inlet system.
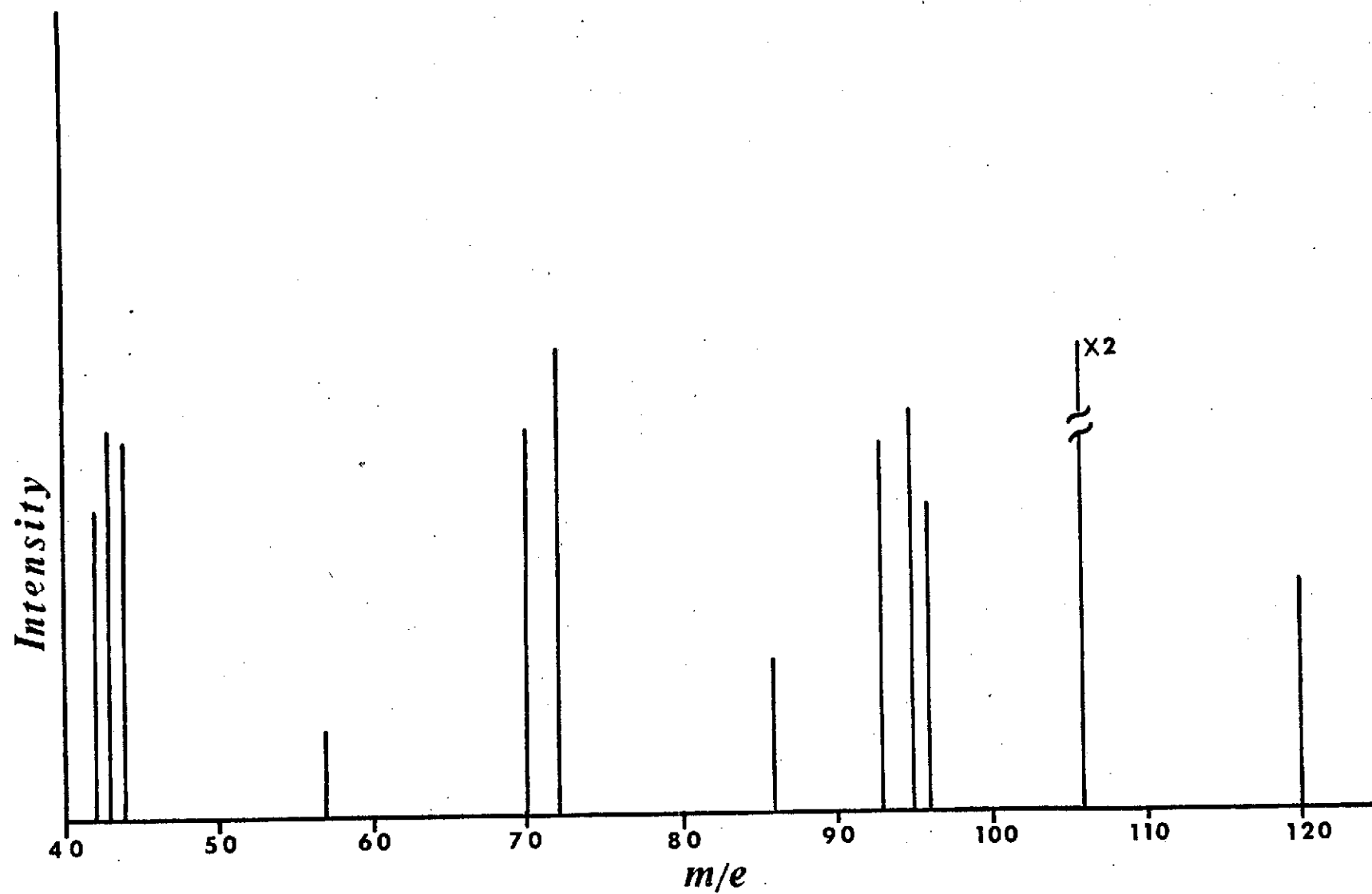
Figure 8. Field ion mass spectrum of air collected using a foam adsorber. Foam temperature during analysis was 100° C.

partial pressure of mercury in the system. However, as is seen

from the total air pollution spectrum, mercury does not confuse

the pattern, whereas the hydrocarbons from an oil diffusion would

add much ambiguity especially where automobile exhaust was involved.

The other major peaks in the background spectrum (Fig. 6) represent

water vapor, nitrogen, oxygen, argon, and carbon dioxide. That is,

the bulk of the background evolved from the foam is representative

of those gases which actually constitute an air background. In

addition, the regions of the mass spectrum which are of interest

for air pollution studies are free of background peaks. Thus the

foam collector can be cleaned so that it does not desorb organic

or hydrocarbon molecules to contribute to the background of an air

pollution sample.

The control spectrum, which was developed by applying field-ion

mass spectrometry to gasoline, is shown in Fig. 7. The seven peaks

shown are in agreement with those observed by others using field ion

mass spectrometry and are typical of the components observed, or

the signature, for gasoline.

An air pollution spectrum for a sample collected in an auto

repair garage is shown in Fig. 8. Field ionization mass spec-

trometry was also employed to analyze this air sample. Thus the

above gasoline control spectrum is applied to identify the origin

of many of the peaks which appear in the total air spectrum. In

fact the bulk of the peaks in the air spectrum collected from the

garage are attributable to gasoline and its by-products. The

additions occur at m/e of 93, 95 and 96, plus the addition of CO_2

at 44.

V. DISCUSSION

A. Selective Permeation Through Membranes

The membrane enricher used in our study was intended to provide for enrichment of the trace compound through a process of selective permeability. The process by which this enrichment occurs is discussed in the following paragraphs.

The permeability constant has units as shown below.

$$Pr = \frac{CC's - Cm \ (\text{membrane thickness})}{Sq \ Cm - Sec - Cm \ Hg \ (\Delta P)}$$

The quantity we are most interested in at any given instant is the ratio of trace contaminant to carrier atmosphere. Consequently, the relative enrichment through a membrane is given by
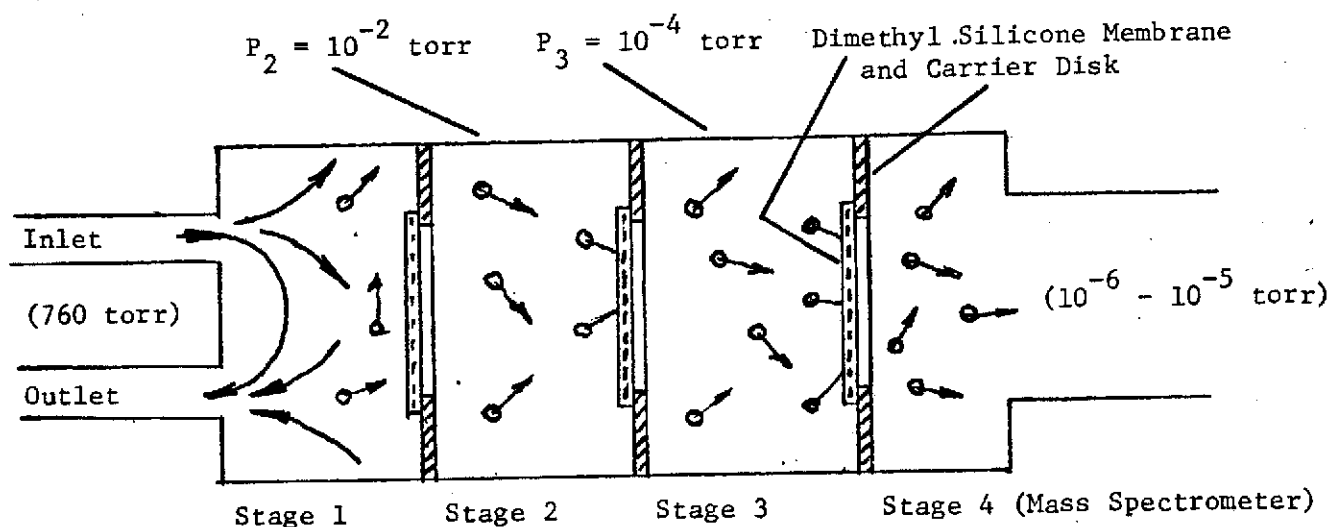
$$\frac{Pr \ (\text{trace contam.}) \ \Delta P \ (\text{trace contam.})}{Pr \ (\text{carrier}) \ \Delta P \ (\text{carrier})}$$

and multiplied by 10^6 gives the concentration in parts per million.

Let us now consider dimethyl silicone rubber as a material for a membrane enricher and 10 ppm SO_2 in N_2 as our example for calculations. The schematic diagram below demonstrates the configuration one might expect for a three stage enricher. We make the following assumptions.

1. One atmosphere exists at the inlet and outlet (7.6×10^{-3} torr SO_2 + 760 torr N_2).

$P_2 = 10^{-2}$ torr $\qquad$ $P_3 = 10^{-4}$ torr $\qquad$ Dimethyl Silicone Membrane and Carrier Disk

Inlet

(760 torr)

Outlet

$(10^{-6} - 10^{-5}$ torr)

Stage 1 $\qquad$ Stage 2 $\qquad$ Stage 3 $\qquad$ Stage 4 (Mass Spectrometer)

2. The flow rate past the membrane is such that the SO_2 is not depleted.

3. The secondcchamber is dynamically pumped to maintain a total pressure of 1×10^{-2} torr.

4. Initially there is no partial pressure of SO_2 in the second chamber.

The permeability constant Pr given by General Electric for SO_2 and N_2 are 1250×10^{-9} and 25×10^{-9} respectively. Thus the relative enrichment is

$$\frac{1250 \times 10^{-9} \times 7.6 \times 10^{-4}}{25 \times 10^{-9} \times 75.9} = 5.0 \times 10^{-4} = 500 \text{ ppm } SO_2 \text{ in } N_2$$

Since the total pressure in the second stage was maintained at 1×10^{-2} torr the partial pressure of SO_2 is 5×10^{-6} torr.

By repeating the calculation across the other two membranes we find 25,000 ppm in stage three and nearly all SO_2 in stage four.

Even though stage four, the entrance to the mass spectrometer, must be maintained at a pressure of 10^{-6} torr the enrichment should be sufficient to allow detection of the trace contaminant.

Certainly not all gases can be expected to have a permeability as great as SO_2. In fact two of the pollutants of interest (CO, NO) have permeabilities of only approximately twice that of N_2. On the other hand CO_2, NO_2 have permeabilities at least an order of magnitude greater than N_2. Furthermore hydrocarbons generally have permeabilities an order of magnitude or more greater than N_2. (Methane, CH_4, has the lowest value being 3 times greater than N_2).

In general for a given compound the permeability constant, Pr, is the product of the diffusivity, D, and the solubility, S, in the membrane material. For dimethyl silicone rubber the diffusivity decreases with increased molecular diameter and the solubility increases with increasing boiling point. However the diffusivity does not decrease significantly with molecular diameters larger than methane (CH_4). On the other hand solubilities continue to increase with boiling point. It is for this reason that hydrocarbons tend to pass so readily.

Because of difficulties in obtaining expected enrichment factors through the three stage enricher we performed some additional more basic tests to determine the actual permeation rates through the membrane material we had available for use.

The data compiled in Table I represents our efforts to verify the permeability factors quoted in the General Electric data

sheet. In all cases, except N_2, O_2 and SO_2, our figures fell considerably below those published. Furthermore the expected enrichment which is obtained by ratioing the permeability factors of any two gases is generally different than that obtained with General Electric data. Our technqque for making these measurements (the time lag method) is the same as that used by other workers including the General Electric laboratory. Since these measurements have been made more than once and on different membranes we are at a loss to explain our discrepancies. Quality control in the production of the membranes themselves may account for our low values.

In Table II we note that in one case we were able to obtain an enrichment factor for the O_2-SO_2 mixture of 40 which is in good agreement with the ratio of permeability factors obtained in our experimental tests. Although the enrichment factors are less in the remaining tests we attribute this to the variation in pressure differential across the membrane face. Of more importance is the fact that we were never able to obtain expected enrichment across the second stage membrane. If the pressure differential across the membrane is a major determining factor for enrichment, then a rather sophisticated pumping system would be required to extract the enriched mixture from the first membrane, raise its pressure and then pass it across the face of the second membrane. Under present circumstances we do not feel that this is a feasible alternative.

Although permeability constants have been published for a large number of compounds, the large majority of work published by General Electric and other independent workers has been on the subject of enrichment of atmospheric oxygen through the membrane. As previously stated, our own efforts to enrich oxygen in the atmosphere proved negative. However we believe that this failure is a result of the enhanced 28 peak due to evolution of gases from the ion pumping system used in the mass spectrometer chamber.

We have made several attempts to determine the origin of our failure to obtain enrichment expected from the ratio of individual permeability factors and several conclusions can be drawn. First, it seems clear that enrichment is a function of both pressure differential across the membrane and flow rate in front of the membrane. For example W.L. Robb[7] points out that maximum enrichment for O_2 in the atmosphere occurs when the low pressure to high pressure ratio is less than .005. Also the fraction of permeating air to air flowing in front of the membrane must be less than .1. More recently, P.L. Valyou[8] has indicated that the minimum pressure ratio must be at least 60 to 1 and that the high pressure side of the membrane is usually run at 175 pounds per square inch pressure.

The variation of permeability with temperature is a variable which we did not determine in our experiments. In this regard, Brubaker and Kammermeyer[6] point out that while a fair amount of permeability data has been published the data in many instances

is for one particular temperature only. The permeability for one temperature is ifficult to interpret since the change of permeability with temperature is essentially unpredictable. Therefore although the General Electric permeativity data are published for conditions of room temperature and pressure it may well be that we could have obtained more satisfactory results had we been able to determine air optimum temperature.

B. Discussion and Conclusions from the Foam Absorber Data

The air pollution spectrum formed by the technology of field ionization mass spectrometry shows a notably reduced number of peaks in comparison to the spectrum generated by electron impact mass spectrometry. (see Fig. 9). The difference is of course not due to any difference in the gases evolved from the foam since both spectra were formed from the effluence of the same type of foam absorbers. The difference is due to a combination of the characteristics of the field ionization technique as compared with the electron impact technique. Fewer peaks in the field ion spectrum of an air sample is partly due to a lower sensitivity for some gas species with this technique, but mostly it is due to the lack of cracking patterns in the field ion case. Thus the technique of field ion mass spectrometry applied to air pollution has shown a much simplier direct analysis of the gases present. While the sensitivity for some gases is lower the spectrum is less ambiguous and yields very good data for hydrocarbons and gasoline pollutants contributed by automobile exhaust.
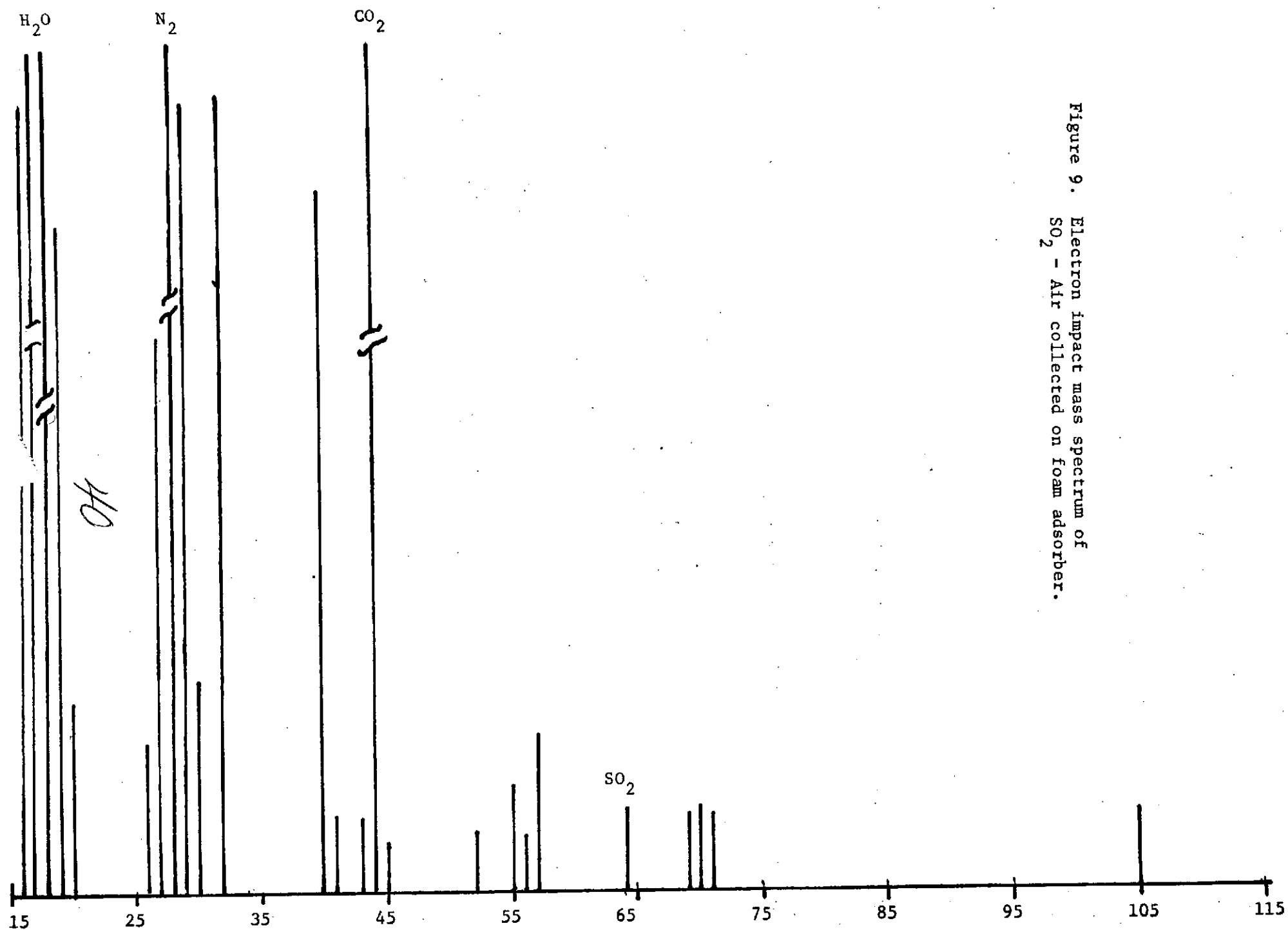
Figure 9. Electron impact mass spectrum of SO_2 - Air collected on foam adsorber.

The results presented above have shown that the polyethylene foam absorber applied to the collection of air pollutants is successful. There are evidences of the retention of some parting of each gas specie from the original sample, i.e. certain species are not eliminated as is the case when membrane separators are employed. The foam absorber also serves very well as an enricher for those components of air which are present in trace amounts and are of interest to the pollution analysis. The amount of N_2, O_2, H_2O and CO_2 retained by the foam is much less in relation to the relative amounts of hydrocarbon and organic molecules. It may be concluded from these data that the polyethylene foam absorber serves well as a remote collector, enricher, and storage unit for air pollution samples.

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